

Supporting Information

Green fabrication of magnetic recoverable graphene/MnFe₂O₄ hybrids for efficient decomposition of methylene blue and the Mn/Fe redox synergetic mechanism

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Sp1. Test of the catalytic activity

The catalytic performances of as-synthesized RGO/MnFe₂O₄ composites were investigated in 50 mL glass beakers with RGO and MnFe₂O₄ as reference. In a typical run, 5 mg of catalyst was added to the solution containing 10 mL of MB dye solution (50 mg L⁻¹) as well as 5 mL of H₂O₂ (30 wt%) solution, and evenly reacted under room temperature with continuous stirring. For a given time interval, 4 mL of the suspension was magnetically separated so as to get supernatant liquid. Afterwards, the

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concentration of MB dye in separated supernatant liquid was determined by UV-vis spectroscopy at 664 nm. Furthermore, in the stability tests of RGO/MnFe₂O₄-75, the catalyst was magnetically separated, washed, dried, and reused in a fresh solution of MB and H₂O₂ after completion of the reaction. Finally, the sample named as RGO/MnFe₂O₄-75-R was collected for further characterization.

Sp2. Analysis of hydroxyl radical (•OH)

The generated active hydroxyl radicals (•OH) were detected by using terephthalic acid (TA) as the probe molecule to evaluate the catalytic properties of the RGO/MnFe₂O₄ composites. Typically, the aqueous solution (25 mL) which involved 5×10^{-4} mol L⁻¹ of TA and 2×10^{-3} mol L⁻¹ of NaOH was prepared. Subsequently, 5 mg of RGO/MnFe₂O₄ was dispersed in the mixture and followed by adding 5 mL of 30 wt% H₂O₂ solution to the mixture. The reactions were carried out under continuous stirring at room temperature. At a fixed interval, the catalyst was separated from the solution with a magnet and 5 mL of the supernatant was used for fluorescence spectrum measurements. After being excited by 325 nm light, the photoluminescence (PL) spectra of the generated 2-hydroxyterephthalic acid were measured at 446 nm.

Sp3. XRD pattern of K₂SO₄ by-product

Fig. S1 shows XRD pattern of the K₂SO₄ by-product collected after the synthesis of experimental 2.1. It is observed that the diffraction peaks including (020), (111), (002), (022), (130), (040), (013), (212), (141), (042), (004), (060) of the obtained product match well with the result of the reported K₂SO₄ (JCPDS NO. 05-0613), indicating that K₂SO₄ obtained from this process is of high purity.

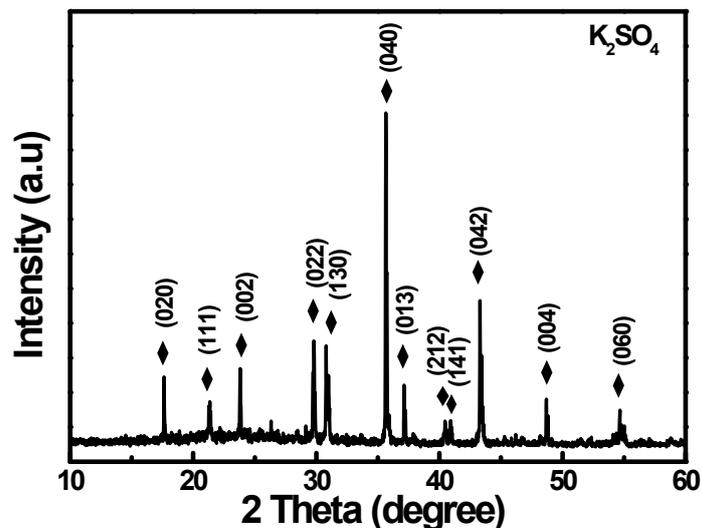


Fig. S1 XRD pattern of the recycled by-product K_2SO_4 .

Sp4. Preparation of Fe_2O_3 , Mn_3O_4 and MnO

Typically, Fe_2O_3 was synthesized via the following steps. First, 1.4 g $Fe(NO)_3 \cdot 9H_2O$ and 0.6g KOH were successively dissolved in 15 mL deionized water under magnetic stirring for 0.5 h. Then, the obtained mixture was placed in a 20 mL Teflon-lined autoclave at 150 °C for 15 h. Finally, the red precipitate was collected by filtration, washed thoroughly with distilled water, and fully dried at 80 °C over night.

Mn_3O_4 was synthesized with the similar method described in the references ^{1,2}. In a typical synthesis, 10 mL of the homogeneous GO/ $MnSO_4$ suspension from modified Hummers method was firstly centrifuged at 8000rpm to get supernatant liquid which contains $MnSO_4$ (0.22 mol L^{-1}). Then 10 mL of KOH (2 mol L^{-1}) solution was added with sufficient oxygen assistance. The system was continuously stirred until the pH value of the suspension reached 12. Finally, the black precipitate was collected by

filtration, washed thoroughly to neutral with distilled water, and fully dried at 80 °C over night.

The MnO was prepared by annealing the above obtained Mn₃O₄ at 500 °C in H₂/Ar (1:9) flow for 4h with the ramp rate of 5 °C.

Sp5. XPS spectra of the cycled RGO/MnFe₂O₄-75-R

To check the variation of the surface chemical properties of the recycled catalyst after Fenton reaction, XPS spectra of the cycled RGO/MnFe₂O₄-75-R were further recorded, as shown in Fig. S2 (a-b). Comparing to the Mn 2p and Fe 2p in Fig. 3 (b - c), the recycled RGO/MnFe₂O₄-75 hybrid exists the same peaks with the fresh one. However, there are some slight differences of the binding energy values of Fe 2p as well as Mn 2p before and after Fenton reaction. As shown in table S1, most peaks of RGO/MnFe₂O₄-75-R shift to lower binding energy values compared with that of the fresh ones. Besides, the full widths at half maximum (FWHM) of the corresponding peaks are broadened and the detailed comparisons of FWHM can be observed in table S2. Such differences may be attributed to the electron transfer of Fe³⁺/Fe²⁺ and Mn³⁺/Mn²⁺ in the catalytic process.

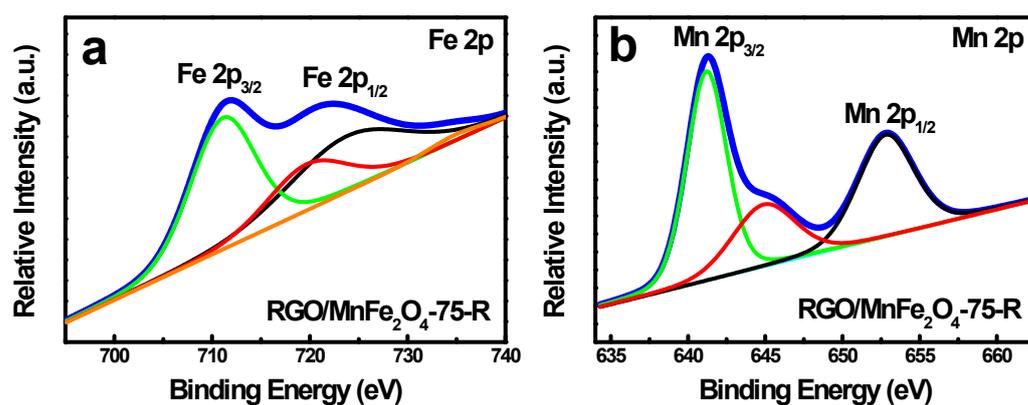


Fig. S2 (a-b) XPS spectra of Fe 2p and Mn 2p regions of RGO/MnFe₂O₄-75-R.

Table S1

Comparisons between Fe 2p and Mn 2p binding energies before and after catalytic reaction.

	Peaks	Before catalytic reaction	After catalytic reaction
Mn 2p	Mn 2p _{3/2} (eV)	641.2	640.7
	Mn 2p _{1/2} (eV)	652.8	652.5
	Satellite peak (eV)	644.9	644.2
Fe 2p	Fe 2p _{3/2} (eV)	711.3	711.1
	Fe 2p _{1/2} (eV)	725.1	723.8
	Satellite peak (eV)	719.8	719.7
	Satellite peak (eV)	733.3	734.8

Table S2

FWHM values for Mn2p and Fe 2p binding energies before and after catalytic reaction.

	Peaks	Before catalytic reaction	After catalytic reaction
Mn 2p	Mn 2p _{3/2} (eV)	3.06	3.26
	Mn 2p _{1/2} (eV)	4.30	5.50
Fe 2p	Fe 2p _{3/2} (eV)	4.36	7.88
	Fe 2p _{1/2} (eV)	3.10	14.21

Sp6. H₂-TPR measurement

H₂-TPR measurement was further applied to investigate the oxidation state of Mn and Fe in the MnFe₂O₄ catalyst with Mn₃O₄ and Fe₂O₃ as the references. The TPR experiments of the obtained samples were carried out in H₂ flow by linearly raising the temperature to 700 °C and the results were shown in Fig. S3. It's noted that all the samples present two peaks in the tested regions. Typically, one peak of Mn₃O₄ located at 300~400 °C region can be assigned to the reduction of Mn³⁺ (Mn₃O₄) to Mn²⁺ (MnO) ². Similarly, the corresponding peaks of Fe₂O₃ centered at 388 and 544 °C result from the reduction process of Fe₂O₃ (Fe³⁺) are related to the formation Fe₃O₄ (Fe³⁺ and Fe²⁺) and FeO (Fe²⁺), respectively ³. Besides, the reduction step of Fe³⁺ to Fe²⁺ starts at a higher temperature (320 °C) comparing with that of Mn³⁺ to Mn²⁺ (210 °C). This observation suggests that Mn³⁺/Mn²⁺ presents higher oxidation capacity than Fe³⁺/Fe²⁺, which is in agreement the reaction described in Eqs. (5). As for MnFe₂O₄ sample, the first peak centered at 432 °C is responsible to the reduction process of MnFe₂O₄ to both MnO and Fe₃O₄. The second one located at 544 °C is attributed to

the similar reduction of iron species in Fe_2O_3 system (from Fe_3O_4 to FeO). Such result is in good agreement with the $\text{Fe}^{3+}/\text{Fe}^{2+}$ and $\text{Mn}^{3+}/\text{Mn}^{2+}$ redox couples that described in the XPS results and provides further evidence to the mechanism.

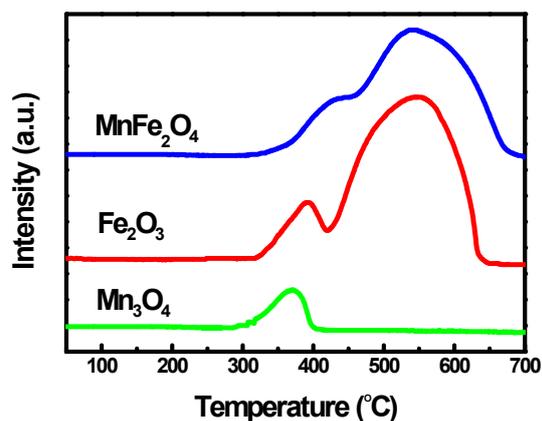


Fig. S3 H₂-TPR spectra of MnFe₂O₄, Mn₃O₄ and Fe₂O₃ samples.

References

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